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**(54) Title: IMPROVED LUBRICANT PERFORMANCE FROM ADDITIVE-TREATED FUELS**

(57) Abstract

A fuel composition improves the antiwear and viscosity controlling properties of an internal combustion engine lubricating oil during operation of the engine. Small amounts of the fuel composition combine with the engine lubricating oil during engine operation and this provides an antioxidant boost to the lubricating oil. Preferably the fuel contains at least 57 g/1000 l (20 lbs/1000 barrels) of a substituted dicyclic aromatic amine which is free of benzylic hydrogen atoms such as a mono- and/or di- $\alpha$ -methyl styrene alkylated phenylenediamine and/or a hindered phenol such as a monostyreneated mono-isobuteneated cresol or di C<sub>16</sub> alkyl phenol. A synergistic effect is demonstrated by a mixture of the aromatic amine and hindered phenol. The fuels used in the composition include gasolines and diesel fuels.

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**IMPROVED LUBRICANT PERFORMANCE FROM  
ADDITIVE-TREATED FUELS**

- This invention relates to a fuel composition containing a concentration of an antioxidant sufficient to improve the performance of an engine oil to which it is exposed during operation of an internal combustion engine, especially to improve the antiwear and viscometric performance of the engine oil.
- The formulation of a lubricant for an internal combustion engine includes the incorporation of an additive package in the lubricant to improve or maintain the properties of the lubricant during service. Commonly used additives include antioxidants, rust inhibitors, antiwear agents, extreme pressure agents, pour point depressants, detergent-dispersants, viscosity control agents, foam inhibitors and the like, as described in Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd Edition, Vol. 14 pp. 477-526.
- The conditions of engine operation tend to degrade the lubricant. Indicators of lubricant degradation include an increase of viscosity of the lubricant, sludge and gum build-up from oxidation of the oil and excessive engine wear. Additives described above are incorporated in the oil to help control these, and other problems, to obtain better overall lubricant performance.
- As engines have increased in power output and complexity, the industry standards for the performance of lubricants and their ability to withstand more rigorous engine operating conditions have become more stringent. Commercially available oils which meet the performance requirements of the API (American Petroleum Institute) Service Classification SG are identified as "SG" oils. This

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classification was recently introduced as a replacement for the SF classification and was established to meet more rigorous performance requirements. The SG oils are designed to minimize engine wear, deposit formation and oil thickening in service. SG oils are intended to improve engine performance and durability when compared to earlier engine oils.

Antioxidant additives may also be used in fuels to improve storage stability, for example, by preventing gum formation. The use of very low concentrations of hindered phenols as antioxidants is known for this purpose. United States Patent No. 5,076,814 discloses fuels containing amounts of tertiary-butyphenols ranging from about 1 to 20 lbs/1000 barrels of fuel (about 0.00041 wt.% to 0.0076 wt.%), as contrasted to the much higher amounts used in lubricants (0.1 to 2.5 wt. %). Butylated hydroxytoluenes are relatively low cost oxidation inhibitors, used in concentrations ranging from about 2 to 3 lbs/1000 barrels of fuel. Use in fuels of an antioxidant performing borated reaction product derived from a hindered phenol in an amount ranging from about 5 lbs/1000 bbl of fuel to 1,000 lbs/1000 bbl of fuel has been described in U.S. Patent Nos. 4,956,105; 4,530,770; and 4,892,563. Borated and metal-containing materials are generally undesirable additives from a regulatory standpoint and a performance standpoint; they are considered harmful to the catalytic converter.

Certain aromatic amines are known for their antioxidant properties in lubricants when used in low concentrations to provide protection for engine parts which are not internally lubricated. For example,

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the use of alkylated diphenylamines in amounts ranging from about 0.05 % to 5% of a lubricant is described in U.S. Patent Nos. 3,773,665; 5,051,198; 5,037,569; 5,024,774 and 4,798,684.

5        Low molecular weight monocyclic aromatic amines such as the substituted 1,6-diaminobenzenes have been used in small amounts in gasolines as stabilizers for stubborn fuels which are not responsive to phenols.

10      Since engine oil compositions tend to deteriorate over time, periodic oil changes are recommended for optimum engine performance and fuel economy. Opinions vary on the recommended frequency of oil changes. The oil change interval can range from about every 2,000 miles to as high as every 15 10,000 miles and even higher, depending upon the type of oil, driving conditions and severity of use. Although frequent oil changes can assure good lubricant performance and freshness of the formulation, eventually the oil will begin to 20 deteriorate before being changed.

25      It would be beneficial to slow the rate of deterioration and to replenish the supply of certain additives by adding small amounts of them to the lubricant during engine operation without adding more oil to the crankcase or changing the oil, either of which may not be possible or feasible. Since, under normal operating conditions, the fuel supply is replenished much more frequently than the oil, it would be beneficial if the fuel could be used to 30 supply fresh additives to the lubricant.

In an automobile engine, small amounts of fuel and fuel additives find access to the engine lubricant during operation. Oil dripping from the value train and power unit flows into a sump located 35 at the bottom of the crankcase. It is circulated by

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a pump through the engine lubricating system. Small amounts of liquid fuel, which remain in the cylinder after combustion, combine with lubricant present on the piston rings and cylinder walls. This lubricant-fuel mixture also flows into the sump to be circulated through the lubricant system or remains on the cylinder for at least a short period of time. A second mode for fuel and fuel additives to find their way to the lubricant is via the blow-by gases, which pass from the combustion chamber, through the narrow gaps in the piston rings, and then into the crankcase--where they can condense or absorb into the oil.

Using a fuel containing a detergent additive to treat a crankcase oil during engine operation is suggested in U.S. Patent No. 3,898,056 to Honnen. The patent proposes that the treated fuel leaking into the crankcase can help disperse sludge and varnish deposits which have built-up in the lubricant. This patent discloses the use of a mixture of high and low molecular weight hydrocarbyl amines in a fuel in small amounts ranging from 150 to 300 weight parts per million (39 to 79 lbs/1000 barrels of fuel).

We have found, however, that formulating fuels with a goal towards treating the lubricant to actually resist degradation of the lubricant, engine wear, and sludge build-up during engine operation, as opposed to dispersing materials already present in the lubricant, is not an easy task. The difficulties encountered include finding an additive which will survive the combustion process intact and still be effective without having any deleterious impact.

Although low molecular weight phenols and certain alkylated amines are known to inhibit fuel

oxidation and gum formation, because of their low molecular weight and higher volatility, they would not be fully soluble in the engine oil; and would be expected to volatilize out of the oil when exposed to  
5 the high temperatures of engine operation.

Thus, it would seem that the high molecular weight fuel additives would be less volatile and, therefore, able to remain in the oil. However, although certain high molecular weight  
10 detergents/dispersants and carrier fluids that are used in gasoline and diesel fuels to control intake valve and fuel injector cleanliness can survive the combustion process, their only expected influence on the engine oil would be as a sludge dispersant, as  
15 mentioned previously.

We found that a fuel composition which contains an antioxidant is capable of improving the performance of a lubricant to which it is exposed during operation of an internal combustion engine.  
20

More particularly, this invention relates to a fuel composition containing an antioxidant additive in an amount sufficient to improve the antiwear and viscosity controlling performance of an engine oil. A typical antioxidant additive contemplated is an  
25 aromatic amine and/or phenol. A particular type of amine antioxidant which has been found to be especially effective when used in this way is a substituted dicyclic aromatic amine which contains no benzylic hydrogen atoms.

The amount of the antioxidant required depends upon the type utilized. For example, we have found that low concentrations of the substituted dicyclic aromatic amines containing no benzylic hydrogen atoms are quite effective as compared to higher  
30

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concentrations of other aromatic amines are required for the same degree of effectiveness.

However, typical effective amounts of antioxidant are at least 14.3 - 57.1 gm/1000 l. (5-10 lbs./1000 barrels) of fuel, more specifically at least 85.7 gm/1000 l. (30 lbs./1000 barrels) of fuel, preferably ranging from over 85.7 gm/1000 l. (30 lbs./1000 barrels) of fuel up to 1142 gm/1000 l. (400 lbs./1000 barrels) of fuel.

We have also found that a synergistic effect results from a mixture of phenol and amine antioxidants such that when they are combined a lower overall concentration of both and a lower concentration of each achieves a better performance than a greater overall concentration of each used individually. We have found that useful relative ratios range, in terms of phenol to amine, from 1:10 to 10:1, specifically, from 1:8 to 8:1, and more specifically, from 2:1 to 5:1.

The molecular weight of the antioxidants is important for purposes of combustion and survivability solubility in the lubricant. The molecular weight is also important so that the antioxidant will be low enough in volatility to remain in the lubricant solution during the high temperatures of engine operation, e.g. -100°C, a typical oil temperature during engine operation. If the molecular weight of the antioxidant is too low, it will volatilize from the lubricant during these high operating temperatures. By contrast, if the molecular weight is too high, it will be unstable and will not survive combustion. For good high temperature stability, the antioxidants should be within a molecular weight range which is comparable to detergents and carrier fluids.

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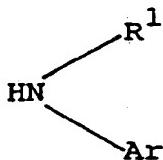
It is believed that these molecules function by providing a time release antioxidant boost to the engine oil during engine operation, particularly in the antiwear and viscosity controlling properties of  
5 the lubricant.

The invention is specifically directed to incorporating an antioxidant, typically an aromatic antioxidant, with a fuel to inhibit engine wear and facilitate viscosity control of a lubricating oil.  
10 During engine operation, the fuel contacts the lubricating oil and supplies the antioxidant to the oil. The specific aromatic antioxidants which we have found to be effective are free of benzylic hydrogen atoms, preferably aromatic amines which are  
15 free of benzylic hydrogen atoms. Specific phenols which we have found effective are hindered phenols. Amounts of these compounds which will demonstrate an effective impact on the lubricant performance are, typically, at least 14.3 - 57.1 gm/1000 l (5-20  
20 lbs/1000 barrels of fuel (0.0002 to 0.0076 wt.%)), ranging from over 85.7 gm/1000 l (30 to 400 lbs/1000 barrels of fuel (0.0114 to 0.1524 wt.%)), preferably the amount ranges from 142.8 gm/1000 l (50 lbs/1000 barrels) of fuel to 856.6 gm/1000 l (300 lbs./1000  
25 barrels of fuel (0.0190 to 0.1140 wt.%) and in most cases from 228.4 to 713.8 gm/1000 l (80 to 250 lbs/1000 barrels) of fuel (0.0305 wt.% to 0.0953 wt.%). Specifically, the amount ranges from 85.7 -  
30 285.5 gm/1000 l (30-100 lbs./1000 barrels) of fuel (0.0114 wt.% to 0.0381 wt.%).

Amine

Representatives of useful amines include aromatic amines, preferably, hydrocarbon substituted aromatic amines. The amine can be represented by the  
35 following structural formula:

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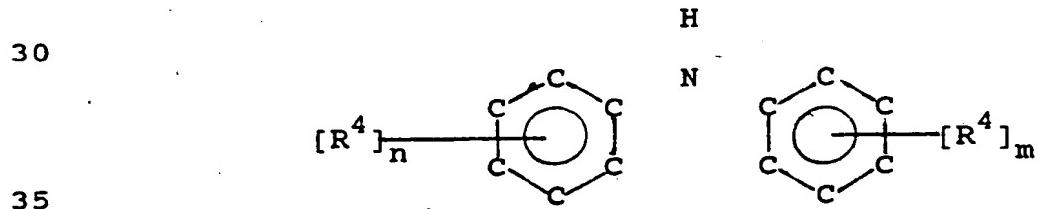


where  $R^1$  is a hydrocarbon group and  $Ar$  is an aromatic hydrocarbon group.

The hydrocarbon group represented by  $R^1$  can be an alkyl, aryl or cycloparaffin. Preferably,  $R^1$  is aromatic.  $R^1$  can contain from 1 to 30 carbon atoms, preferably from 1 to 20 carbon atoms. There can be a hydrocarbon group bonded to  $R^1$  and this hydrocarbon group can be alkyl, alkenyl, aralkyl, aryl, or alkaryl having from 1 to 30 carbon atoms, preferably from 4 to 20 carbon atoms. The hydrocarbon groups represented by  $R^1$  can be in any isomeric arrangement, that is, the hydrocarbon can be straight chain or branched chain.

Representative examples of aromatic groups represented by  $Ar$  include aryl or alkaryl having from 6 to 30 carbon atoms, preferably from 10 to 25 carbon atoms.  $Ar$  can contain a hydrocarbon substituent which can be an alkyl, aryl, alkaryl or aralkyl group. The substituent group can contain from 1 to 30 carbon atoms, preferably from 4 to 20 carbon atoms and can be straight chain or branched.

Preferably, the aromatic amine is a substituted dicyclic aromatic amine in which  $R^1$  and  $Ar$  are alkylated aromatic groups. This amine can be characterized by the following structural formula:

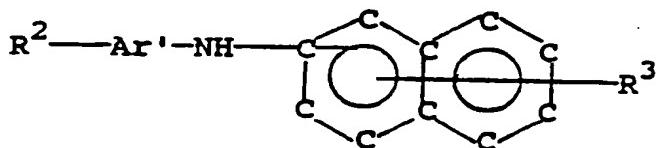


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Where R<sup>4</sup> is a hydrocarbon substituent containing from 4 to 30 carbon atoms, preferably from 8 to 20 carbon atoms, n ranges from 0 to 1 and m ranges from 0 to 1, the sum of n and m is at least 1. Mixtures of 5 dialkylated amines (where the sum of n and m is 2) and minor amounts of trialkylated amines (where the sum of n and m is 3) are also contemplated.

Particularly preferred amines are those that are free of benzylic hydrogen atoms. A representative 10 example of such an amine which has demonstrated excellent performance is a substituted dicyclic aromatic amine as described above in which R<sup>4</sup> contains the radical C<sub>6</sub>H<sub>5</sub>R<sup>5</sup>, where R<sup>5</sup> is a tertiary hydrocarbon group; that is, the carbon atoms of the 15 hydrocarbon are in any isomeric arrangement provided that the carbon atom bonded to the aromatic is bonded to at least two other carbon atoms or hydrocarbon groups.

Substituted naphthylamines are expected to be 20 useful. Amines falling within this category are those in which R<sup>1</sup> is a naphthyl substituent and Ar is an alkyl or alkenyl substituted aromatic hydrocarbon. These can be represented by the following structural formula:



25 where R<sup>2</sup> is an alkyl or alkenyl group having from 1 to 30 carbon atoms, preferably 4 to 20 carbon atoms, Ar' is phenyl or naphthyl and R<sup>3</sup> is a hydrogen atom or a hydrocarbon group which can be alkyl, aryl or alkaryl.

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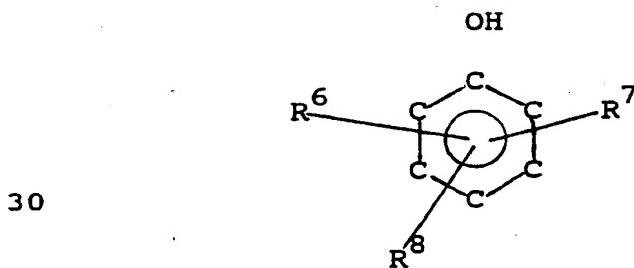
For purposes of high temperature stability, the amines should have molecular weights of at least about 250, ranging from 150 to 1500, preferably from 200 to 1000, and even more preferably from 250 to 5. 500.

Representative examples of the foregoing amines include diphenyl amine, phenyl tolyl amine, ditolyl amine, dioctyldiphenylamine, butyl diphenylamine, octyldiphenylamine, di-alpha- or beta-naphthylamine, phenyl alpha- or beta-naphthylamine, butyl-alpha naphthylamine, phenyl-beta-naphthyl amine, tolyl naphthyl amine, dicyclohexyl amine, N-phenyl butyl amine, N-phenyl octyl amine, diphenyl para-phenylenediamine, mixtures of mono- and di-heptyl diphenylamines, mono- and di-hexadecyl diphenylamines, N-phenyl, N-4-(alphamethylstyryl) phenylamines and the like.

Particularly preferred amines include mono- $\alpha$ -methyl styrene alkylated diphenylamine, di- $\alpha$ -methyl styrene alkylated diphenylamine and mixtures of mono- and di- $\alpha$ -methyl styrene alkylated diphenylamines and nonylphenyl-alpha-naphthylamine.

Phenol

Specific phenols are represented by the 25 following structural formula:



where R<sup>6</sup> and R<sup>7</sup> are the same or different hydrocarbon group containing from 1 to 50 carbon atoms,

preferably from 4 to 12 carbon atoms, even more preferably from 4 to 8 carbon atoms.  $R^6$  and  $R^7$  can also contain heteroatomic groups such as N, O and S.  $R^6$  and  $R^7$  can be in any isomeric arrangement i.e.,  
5 straight chain, branched chain or aromatic. At least one of  $R^6$  or  $R^7$  can be a tertiary hydrocarbon group, preferably both are tertiary hydrocarbon groups.  $R^8$  can fall within any of the above definitions of  $R^6$  and  $R^7$  or  $R^8$  can be a hydrogen atom. Where any  
10 hydrocarbon is tertiary, the carbon atoms of the hydrocarbon groups can be in any isomeric arrangement provided that the carbon atom bonded to the phenol is bonded to at least two other carbon atoms or hydrocarbon groups. Hydrocarbon groups represented  
15 by R can be alkyl, alkenyl, cycloparaffin, aryl, alkaryl or aralkyl.

Relatively high molecular weight phenols demonstrate satisfactory results. They can survive the combustion process and not volatilize from the  
20 lubricating oil during high temperature engine operation. Phenols contemplated should have a molecular weight of at least 150 ranging to 1500, preferably 200 to 1000 and more preferably from 250 to 500.

25 A mixture of phenols falling within the above definition is also contemplated. Specifically, alkylated phenols which contain a range of carbon atoms in the hydrocarbon substituents, can be prepared from a commercial mixture of  $C_4$  to  $C_{20}$  olefins such that the final product will contain  
30 alkylated phenols in which the alkyl groups of the phenols range from 4 to 20 carbon atoms.

Specific examples of contemplated hydrocarbon groups represented by  $R^6$ ,  $R^7$  and  $R^8$  include methyl,  
35 ethyl, propyl, butyl, tert-butyl, pentyl, hexyl,

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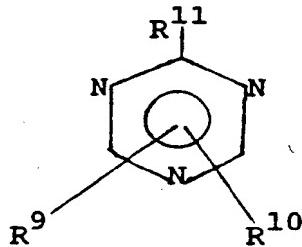
heptyl, octyl, nonyl, decyl, dodecyl, tetradecyl, hexadecyl and octadecyl or higher hydrocarbon groups and any combination thereof including dialkylphenols such as di-C<sub>16</sub>-alkylphenol.

5 In a particularly preferred embodiment the phenol is a hindered phenol in which the hydrocarbon groups attached to the phenol, R<sup>6</sup>, R<sup>7</sup> and optionally R<sup>8</sup>, are spatially arranged about the OH group of the phenol to prevent or retard reaction with other 10 molecules.

The hindered phenols include, but are not limited to, cresol (methylphenol); monostyreneated, mono-isobuteneated cresol, butylated hydroxy toluenes, i.e., 4,4'-methylenebis-(2-6-di-t-butylphenol).

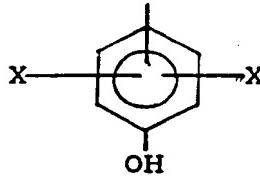
A specific example of a phenolic antioxidant which may also find utility in this invention is represented by the following structural formula:

20



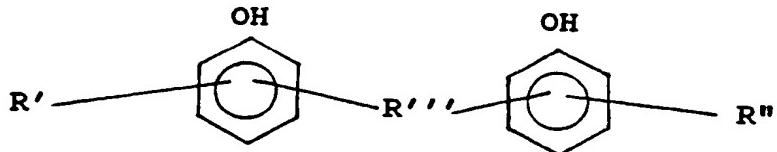
25 in which R<sup>9</sup>, R<sup>10</sup> and R<sup>11</sup> are each hindered phenolic groups having the structural formula

30



where X represents a hydrocarbon group containing from 1 to 30 carbon atoms.

Also contemplated are alkylated bisphenols represented by the structural formula



5 where R' and R'' are alkyl groups ranging from 1 to 30 carbon atoms. R''' is a lower alkyl group, either straight chain or slightly branched chain, and, typically, R''' is any of the following groups -CH<sub>2</sub>-,-C(CH<sub>3</sub>)<sub>2</sub>- or -CH<sub>2</sub>-CH(CH<sub>3</sub>)-. Phenols of this kind are  
10 commercially available.

The concentration of the antioxidant in the fuel should be sufficiently high to improve the properties, particularly the antiwear and viscometric properties, of the lubricant to which the fuel is exposed during engine operation. Since it is estimated that only 5 to 20% of the antioxidant remains unburned after fuel combustion to find its way to the engine lubricant oil (depending upon the structural configuration of the antioxidant), the  
15 20 antioxidant concentration is high relative to the amount usually employed for fuel stability purposes.

The fuels contemplated include gasoline and diesel fuels. The fuels contemplated are petroleum distillate fuels, typically, having an initial  
25 boiling point above 24°C (75°F) to 57°C (135°F) and an end boiling point from 121°C to 399°C (250°F to 750°F). Specifically, the fuel compositions contemplated include gasoline base stocks such as a mixture of hydrocarbons boiling in the gasoline  
30 boiling range which is from 32°C (90°F) to 204°C (400°F). This base fuel may consist of straight chain, branched chain or cyclic hydrocarbons: paraffins, cycloparaffins, olefins, aromatic hydrocarbons, or mixtures thereof. The base fuel can

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be derived from sources such as, straight run naphtha, alkylate, or from catalytically cracked or thermally cracked gasoline or reformate. The composition and octane level of the base fuel are not 5 critical and any conventional motor fuel base can be employed in the practice of this invention.

Other fuel compositions contemplated include distillate fuels and this is not intended to be restricted to straight-run distillate fractions. 10 These distillate fuels can be straight-run distillate fuels, catalytically or thermally cracked, or hydrocracked distillate fuels, or other distillate components. The distillate fuels specifically contemplated are road diesel and/or marine fuels. 15 These diesel fuels boil in the range from 166°C to 399°C (330°F to 750°F) with the end point ranging from 227°C to 343°C (440°F to 650°F), usually the end boiling point is not more than 371°C (700°F). Road diesel fuels, as opposed to marine diesel fuels are 20 preferred.

The fuels can be treated in accordance with well-known commercial methods, such as mercaptan extraction or oxidation, hydrofinishing, etc.

The fuels may include oxygenate components such 25 as alcohols and/or ethers, for example, hydrocarbon fuels which contain oxygenates in amounts of up to about 50% volumes per volume. Typical examples of such oxygenated fuel components are methanol, ethanol and mixtures of methanol and ethanol, 30 diisopropylether (DIPE), isopropanol (IPA), methyl-tert-butyl ether (MTBE) or tert-amyl-methyl ether (TAME).

The fuel compositions of the instant invention may additionally comprise lower concentrations of 35 additives which are generally employed in fuel

compositions. Thus, compositions of the (instant) invention may additionally contain conventional carburetor detergents, anti-icing additives, co-antiwear additives, detergents and co-antioxidants.

5       The kinds of engine lubricants likely to benefit from fuels treated in accordance with this invention include liquid oils in the form of either a mineral oil, hydrocracked oil, synthetic oil or mixtures thereof which are used as engine lubricants. In  
10      general, the oils include both paraffinic and naphthenic components. The lubricating oils are of a suitable lubrication viscosity range to comply with engine oil specifications, for example, as set by the SAE, e.g. single grade oils such as 30, 40, 50, 5W,  
15      10W grade or multigrade oils such as 10W-30, 5W-30, 10W-40, 15W-40, etc. Base oil viscosities may typically range, for example, from 6 mm<sup>2</sup>/s (45 SUS) at 38°C (100°F) to 1500 mm<sup>2</sup>/s (6000 SUS) at 38°C (100°F), and preferably from 7.5 to 54 mm<sup>2</sup>/s (50 to  
20      250 SUS) at 99°C (210°F). Viscosity indexes from about 95 to 130, and even higher, being preferred.

Where synthetic oils, or synthetic oils employed as the vehicle for the grease are desired in preference to mineral oils, or in mixtures of mineral  
25      and synthetic oils, various synthetic oils may be used. Typical synthetic oils include polypropylenes, polyisobutylenes, polybutenes, polydecenes and other polyalpha olefin lubricating fluids used in engine oils.

30      The lubricating oils can contain other additives generally employed in lubricating compositions such as corrosion inhibitors, detergents, extreme pressure agents, viscosity index improvers, friction reducers, antiwear agents and the like.

Evaluation of the Invention

5       The performance of a lubricant used in an engine supplied with a gasoline containing different dosages of antioxidant was evaluated in the Sequence IIIE Engine test. The Sequence IIIE test is one of the tests designed to evaluate the performance characteristics of an engine oil to determine whether it qualifies for API (American Petroleum Institute) Service Classification SG.

10      The API Sequence IIIE engine oil test allows evaluation of the high-temperature wear, oil thickening and deposit protection capabilities of SG engine oils. The Sequence IIIE test particularly focuses on wear protection and oil thickening control. The IIIE test uses a 3.8L Buick V-6 engine which is operated on leaded fuel at 3000 rpm for a maximum test length of 64 hours.

15      The test is terminated if the oil level reaches 0.8 kg (28 ounces) low before 64 hours of operation or it is terminated after 64 hours of operation. The viscosity is measured in terms of percent viscosity increase versus engine operating time. For service classification SG, a maximum 375% viscosity increase measured at 40°C after 64 hours is allowed.

20      The following are the standards of performance results established by the test:

Average Sludge	9.2 (min)
Piston Skirt Varnish	8.9 (min)
Oil Ringland Deposits	3.5 (min)
Cam & Lifter Wear ( $\mu$ m)	
Average	30 (max)
Maximum	62 (max)

25      Thus, the Sequence IIIE test evaluates the high-speed, high temperature oxidation, wear and deposit

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forming tendencies of motor oils for gasoline engine service.

During the test the engine was run for 64 hours at constant speed and load, with a shutdown every 5 eight hours for oil sampling and leveling. The following operating conditions were maintained.

Speed, RPM	3,000 ± 20
Oil Temp., °C (°F)	149 ± 1.1 (300 ± 2)
Coolant outlet Temp., °C (°F)	115 ± 1.1 (239 ± 2)
10 Coolant inlet temp., °C (°F)	110 ± 1.1 (230 ± 2)
Blow-by, l/sec.	
(cu.ft./min.)	0.76 ± 0.09 (1.6 ± 0.2)
Power, joules/sec. (BHP)	50558 ± 1491 (67.8 ± 2)
Air/Fuel ratio	16.5 ± 0.5
15 Air inlet temp., °C (°F)	27 ± 1.5 (80.6 ± 2.7)
Humidity, mg/gm (grains/lb)	
dry-ai	11.4 ± 0.7 (80 ± 5)

The engine lubricating oil used in the test was a 10W-30 mineral oil (based) lubricant containing a 20 typically detergent/dispersant inhibitor additive package.

Example 1

Two alkylated diphenyl amines (DPAs) were tested in the Sequence IIIE test. (1) a di-C<sub>16</sub> diphenyl 25 amine (di-C<sub>16</sub>-DPA), which contains benzylic hydrogen atoms, was designated Additive A; and (2) a liquid mixture of mono- and di- $\alpha$ -methyl styrene substituted diphenylamines which are free of benzylic hydrogen atoms, was designated Additive B.

30 The following Table 1 sets forth the results of the test.

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Table 1  
Sequence IIIE Engine Test

Additive	Dosage g/1000 l (lb/1000 barrels)	Cam & Lifter Wear ( $\mu\text{m}$ )	% Lubricant Viscosity Increase
5	----	37.8	911
	A 143 (50)	19.2	713
	A 714 (250)	3.2	52
	B 254 (89)	3.7	39
	B 128 (45)	38.2	26
	B 86 (30)	12.8	236

10           The data show that the fuel treated with additive A or B significantly impacted the lubricant performance. The treated fuel, as compared to the untreated fuel, resulted in reduced cam-shaft and lifter wear and reduced oil thickening. A 15 concentration of 254 g/1000 l (89 lb/1000 barrels) of fuel of Additive B exceeded the API viscosity increase requirements of the SG classification. While low dosages of Additive A, whose molecular weight is about 50% higher than Additive B, failed to 20 meet the viscosity increase requirement of 375% for the SG classification, a higher dosage of 714 g/1000 l (250 lbs/1000 barrels) of additive A exceeded the requirements for the SG classification, achieving a performance comparable to Additive B. It is not 25 entirely understood why such high concentrations of the higher molecular weight antioxidant are required; however, one explanation is that this antioxidant is less stable at the high temperatures of combustion than Additive B.

30           As also demonstrated by the data of Table 1, relatively low concentrations of Additive B achieved effective results. A concentration of 86 g/1000 l

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(30 lbs/1000 barrels) resulted in an acceptable 12.8  $\mu\text{m}$  wear measurement. (The wear measurement of 38.2  $\mu\text{m}$  at 128 g/1000 l (45 lbs/1000 barrels) indicated failure of test engine parts and was not attributable to the lubricant). There was a significant % change in viscosity in going from 128 g/1000 l to 86 g/1000 l (45 lb/1000 barrels to 30 lb/1000 barrels) indicating that the antioxidant concentration was important for maintaining lubricant viscosity.

**10 Example 2**

This example demonstrates the performance of the phenolic antioxidants in the Sequence IIIE test. Additive C was a di-C<sub>16</sub>-alkyl phenol. Additive D was a monostyreneated, mono isobuteneated cresol (Uniroyal's Naugard 529) and Additive E was a mixture of 31 g/1000 l (11 lbs./1000 barrels) of Additive B (the mixture of mono- and di- $\alpha$ -methyl styrene substituted diphenylamines of Example 1) and 106 g/1000 l (37 lbs./1000 barrels) of Additive C.

20

**Table 2**

Additive	Dosage g/1000l (1b/1000 barrels)	Cam & Lifter Wear ( $\mu\text{m}$ )	% Lubricant Viscosity Increase
---	---	37.8	911
C	357 (125)	9.9	90
D	163 (57)	12.7	306
E	137 (48)	9.4	57

As the data of Table 2 show, at relatively low dosages, effective wear and viscosity increase protection was achieved with the phenolic antioxidants. The data also show, comparing Tables 1 and 2, that a mixture of phenol and amine antioxidants was more effective for inhibiting wear

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and maintaining a low viscosity at a lower dosage than the phenol or the amine antioxidants used alone which indicates a synergistic effect.

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**CLAIMS:**

1. An internal combustion engine fuel comprising a major amount of an internal combustion engine fuel and an antioxidant in an amount of at least 5 231 g/1000 l barrels of fuel sufficient to improve the antiwear and viscosity properties of a lubricant oil to which the fuel is exposed during operation of the internal combustion engine.
- 10 2. The composition of claim 1 in which the antioxidant is an aromatic amine which has the structural formula:



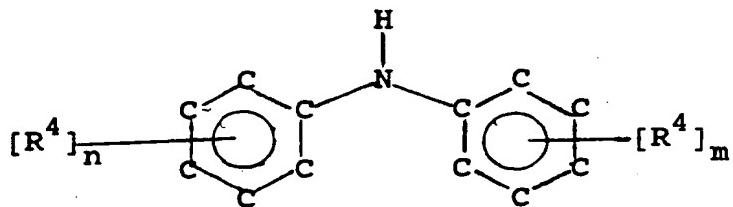
15 where R<sup>1</sup> is a hydrocarbon group containing from 1 to 30 carbon atoms and Ar is an aromatic hydrocarbon containing from 6 to 30 carbon atoms.

- 20 3. The composition of claim 2 in which the aromatic amine is a substituted dicyclic aromatic amine.
4. The composition of claim 2 in which the aromatic amine is free of benzylic hydrogen atoms.

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5. The composition of claim 3 in which the amine has the following structural formula:

5



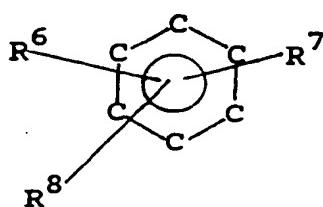
10 where  $R^4$  is a hydrocarbon substituent containing from 4 to 24 carbon atoms, n ranges from 0 to 1 and m ranges from 0 to 1, the sum of n and m is at least 1.

15 6. The composition of claim 5 in which  $R^4$  contains the radical  $C_6H_5R^5$  in which the group represented by  $R^5$  is a tertiary hydrocarbon group.

20 7. The composition of claim 2 in which the amine is dihexadecyl-diphenylamine, mono-alpha-methyl styrene alkylated phenylenediamine, di-alpha-methyl styrene alkylated phenylenediamine or a mixture of mono- and di-alpha-methyl styrene alkylated phenylenediamine, phenyl naphthylamines.

8. The composition of claim 1 in which the antioxidant is a hindered phenol or hindered bis-phenol having the structural formula:

5



10 where R<sup>6</sup> and R<sup>7</sup> are the same or different hydrocarbon group containing from 1 to about 50 carbon atoms, R<sup>8</sup> is a hydrocarbon group containing from about 1 to about 50 carbon atoms or R<sup>8</sup> is a hydrogen atom.

15 9. The composition of claim 8 in which the molecular weight of the phenol ranges from about 150 to 1500.

10. The composition of claim 8 in which at least one of R<sup>6</sup> or R<sup>7</sup> of the phenol is a tertiary hydrocarbon group.  
20

11. The composition of claim 1 in which the phenol is an alkylated bisphenol.

12. The composition of claim 8 in which the hindered phenol is used in an amount of about 114 gm/1000  
25 l of fuel to 857 gm/1000 l of fuel.

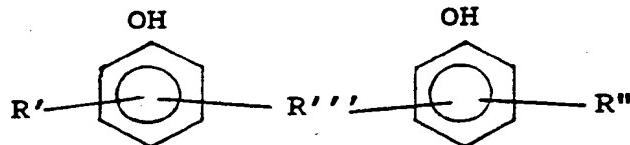
-24-

13. The fuel composition of claim 8 in which the hindered phenol is 4,4-methylenebis(2-6-di-t-butylphenol) or alkylated derivatives, di-C<sub>16</sub>-alkylphenol or monostyreneated monoisobuteneated cresol.

5

14. The full composition of claim 8 in which the hindered bis-phenol is an alkylated bisphenol which has the structural formula:

10



where R' and R'' are alkyl groups containing 1 to 30 carbon atoms and R''' is a lower hydrocarbon group.

15

15. The fuel composition of claims 1, 2, 3, 4, 5 or 6 wherein the antioxidant is a mixture of a hindered phenol antioxidant and an aromatic amine antioxidant.

20

16. The fuel composition of claim 15 in which the hindered phenol is a hindered bisphenol.

17. The fuel composition of claim 15 in which the hindered phenol is a monostyreneated mono-isobuteneated cresol.

25

18. The fuel composition of claim 15 in which the aromatic amine is a substituted dicyclic aromatic amine.

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19. The fuel composition of claim 18 in which the substituted dicyclic aromatic amine is a methyl styrene-substituted diphenylamine.
- 5 20. The fuel composition of claim 15 in which the relative ratio of phenol to amine ranges from 10:1 to 1:10.
21. The composition of any of the preceding claims in which the fuel is a gasoline or diesel fuel.

## INTERNATIONAL SEARCH REPORT

I. National application No.

PCT/US94/03558

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : C10L 1/22; 1/18

US CL : 44/424, 426, 428, 429, 430, 432, 450

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 44/424, 426, 4229, 430, 432, 450

; IPC(5): C10L 1/22, 1/18

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A, 3,035,015 (Spacht) 15 May 1962, col. 1, lines 10-11 and 19 - end, and col. 2, lines 32-49.	8-17 and 20-21
Y	US,A,3,217,040 (Schmerling) 09 November 1965, col. 1, lines 14-30, col. 2, lines 15-58.	2-7 and 15-21
X ----	US,A,3,404,087 (Scoggins) 01 October 1968, col. 1, lines 42-col. 2, lines 1-end and col. 3, lines 1-22.	1 and 21 -----
Y	US,A,3,556,748 (Stedman) 19 January 1971, col. 1, lines 15-23 and 53-col. 2, lines 1-57 and col. 3, lines 45-54.	1-21 2-7 and 15-21

Further documents are listed in the continuation of Box C.  See patent family annex.

* Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)		
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
11 MAY 1994	JUN 15 1994

Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer  MARGARET B. MEDLEY Telephone No. (703) 308-2518
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Form PCT/ISA/210 (second sheet)(July 1992)\*

**INTERNATIONAL SEARCH REPORT**

I national application No.  
PCT/US94/03558

**C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,3,839,210 (Beiswanger) 01 October 1974, col. 1, lines 42-col. 2, lines 1-end and col. 3, lines 1-22.	1-5,8-12 and 14-21
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Y		1-21

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